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Synthesis and Characterization of a Homogeneous Cobalt Catalyst for the Hydrogenation of Acetone to Isopropanol

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SYNTHESIS AND CHARACTERIZATION OF A HOMOGENEOUS COBALT CATALYST FOR THE HYDROGENATION OF ACETONE TO ISOPROPANOL

by

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ABSTRACT

To lessen environmental strain and decrease dependency on noble metals for catalysis, first-row metals are continuously being explored as alternative catalysts for reactions of interest, particularly those that close the carbon cycle or promote fuel production. Recently, homogeneous cobalt catalysts have been shown to be viable options for effective hydrogenation of C-O double bonds, with cobalt-triphos being of particular interest. Here, we report the characterization of synthesized a cobalt-triphos complex by nuclear magnetic resonance spectroscopy and optical spectroscopy. Analysis of the electrochemistry of the cobalt-triphos complex suggests promising electrocatalytic capability for the hydrogenation of acetone to produce isopropanol.

INTRODUCTION

Hydrogenation of unsaturated C-C and C-O bonds are pivotal reactions in several commercial processes. Pharmaceutical manufacturers and food production companies often rely on reactions that functionalize and defunctionalize hydrocarbons and other fossil-fuel derived species. These industries employ hydrogenation catalysts to transform ketone functional groups (C-O double bonds) to alcohol functional groups[1]. A selective, efficient way to hydrogenate C-O bonds is essential for the future of these important industries.

Likewise, the energy industry is in search of efficient modes of reducing carbon dioxide (again, a C-O double bound) into species such as formate or methanol, that can be used as fuel. The seasonal and daily variation of solar power requires that solar photovoltaic devices are paired with energy storage systems, such as batteries or chemical fuels. Electrocatalytic chemical fuel production is more atom and energy efficient than most battery applications.

The hydrogenation of C=O double bonds (example in **Figure 1)** can convert lesser value or environmentally harmful species into useful feedstocks and fuels. The conversion of carbon pollutants into useful fuels allows for the closing of the carbon cycle, suggesting a sustainable alternative to petroleum-based fuel.[2]

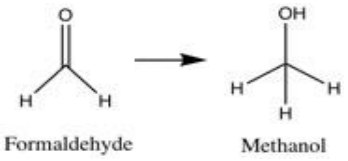

Figure 1. An example of hydrogenation reaction in which the C-O double bond is then saturated with H-bonds.

In an idealized device, solar energy would be converted into a carbon-based chemical fuel, which upon burning, would produce CO_2. The carbon dioxide produced would be trapped by the device, and with the captured solar energy, would be converted yet again into chemical fuel.

Homogenous electrocatalysts are of particular interest in sustainable chemistry.[3] Particularly, homogeneous cobalt catalysts may provide viable alternatives for sustainable production of fuels.[4567] These catalysts might also help in reducing the use of unsustainable carbon sources. The use of non-noble metal catalysts provides a possibility of equally efficient alternatives to former modes of catalysis. As compared to noble electrocatalysts, these alternatives are traditionally less successful at performing desired reactions due to susceptibility to decomposition and the low performance of selectivity for the reaction of interest due to the many active competing reactions in the controlled setting. Similar to the proposed catalyst, $[Co(triphos)]BF_4$ (Triphos=1,1,1-tris(diphenylphosphinomethyl)ethane), has been proven to be successfully synthesized and useful catalytically for the conversion of CO_2 to methanol, but thermochemically at high temperatures and pressures.[8] This project hopes to promote the hydrogenation of C=O bonds at ambient temperatures and pressures electrochemically with a Co-Triphos complex.[9-10]

Traditionally, hydrogenation catalysis has been done with heavier, expensive metals like platinum[11] on carbon, iridium[12], and rhodium[13]. These metals are in low abundance and require significant ecological cost to cobalt. Development of efficient cobalt catalysis would allow for cheaper and more accessible hydrogenation, and therefore fuel production.[14]

For the specific hydrogenation reaction here (the conversion of acetone to isopropanol), the viability of catalytic reactions at low to moderate temperatures and ambient pressures would also generate a more economically favorable method of production for isopropanol, a high value chemical ($1,555/MT),[15] from the lower value feedstock of acetone ($1,327/MT).[16] Furthermore, successful hydrogenation of acetone to isopropanol may provide supplemental insight on the hydrogenation of other C-O bonds applicable to the development of a sustainable, clean form of energy.[17]

When a first-row metal complex is used, a different mechanism is used, which may produce unwanted side products or not be as energy efficient. Despite this, these metals pose an opportunity. The proposed mechanism for this project is illustrated in **Figure 2**. In this, the cobalt metal can be reduced and protonated, and reduced again to generate a hydride ligand with sufficient hydricity to reduce to a C=O double bon.

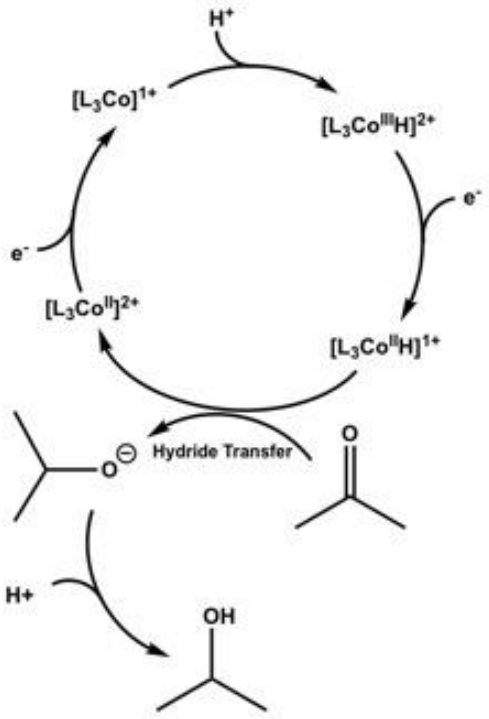

Figure 2. Proposed cobalt mechanism highlighting the catalytic capability of the metal-hydride complex.

To be a successful electrocatalyst, the reaction should proceed with a high turnover number, a high turnover frequency, and a little-to-no overpotential. Overpotential is defined as the additional potential beyond the thermodynamic potential needed to drive the reaction at a certain rate.[18] This difference in potential is visualized in **Figure 3.** High overpotential is then understood as wasted electrical potential. In the absence of a catalyst, hydrogenation reactions are often not observed. The reaction can be lethargic at ambient temperatures and pressures,[19] and while increased voltages can generate products, a small overpotential will result in faster product formation with more efficient use of energy.

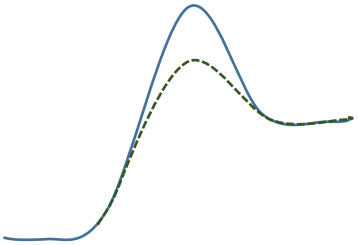

Figure 3. Overview of overpotential for a reaction that is thermodynamically unfavorable – The blue line is the normal activation energy for the reaction and the green dotted line is the catalytic reaction in which a good catalyst has a lower slope in the energy pathway.

Turnover number, on the other hand, is defined as the number of product molecules formed by every catalyst molecule in the solution.[20] To be economically viable on an industrial scale, the turnover number must be considerably high, indicating that the catalyst is long-lived and not particularly susceptible to decomposition during catalysis. Environmentally speaking, the successful electrocatalyst that has a high turnover number will also decrease production waste and promote a greener alternative for chemical production.

Turnover frequency is a measure of the speed of the reaction: the faster the catalyst generates product, the higher the turnover frequency. It is reported as the amount of product generated from the reaction of interest per unit of time but can also be measured as a function of the current consumed by an electrocatalyst. This will also decrease the amount of catalyst that is required for the reaction, therefore further decreasing the environmental strain of production.

Selectivity of the catalyst must also be addressed - the catalyst must be functional and react so that it can control the pathway for the reaction without generating unwanted byproducts. Highly active catalysts are desired for increasing the turnover number and frequency, but it must be controlled so that

catalyst only affects the reaction of interest. Homogeneous catalysts must provide the lowest energy configuration to promote the desired reaction.[21]

Synthesis of the desired HCoTriphos complex was modeled after previous reports that coordinated triphos to cobalt from $[Co(H_2O)_6](BF_4)_2$ starting material in equimolar amounts.[22-23] Sacconi and co-workers reported successful synthesis of the desired trigonal-pyramidal complex analog $[CoH(np_3)]$ (np_3=tris(2-diphenylphosphinoethyl)amine) with the same $[Co(H_2O)_6](BF_4)_2$ starting material.[24-25] This research observed that the coordination of the ligand to the metal salt will preferentially form the hydride complex.

The coordination of the triphos ligand was modeled after this synthesis to produce the same hydride complex. The outer shell coordination by BF_4 ions will also allow for better structural support for catalysis. This mode of synthesis provided an open site at the metal center capable of coordinating a dihydride species. Synthesis was then performed with the proposed methods by Enamullah[26] and Marinescu,[27] in which both projects used $NaBH_4$ to reduce the complex and add a hydride ligand to the metal. Characterization of this synthesized cobalt compound was performed using UV-Vis and H^1-NMR techniques. Characterization of HCoTriphos by Marinescu was used as comparative literature; characterization of HNiTriphos by Kourkine was used as comparative literature.[28]

Observation of this metal hydride and study of its hydricity also allows for a better understanding of the reactivity. Previous research on this Co-Triphos complex suggests that hydrogen is produced by this metal in an electrochemical cycle where Co^{III} is reduced to Co^{II}. [29] In this study, p-toluenesulfonic acid is used to understand offset hydrogen production and understand the kinetics of the HCoTriphis catalyst. Through the study of the synthesized metal complex, the catalytic nature of the product, as shown by catalytic CV currents, in response to acetone, could also be measured. The mechanism of interest would then be better understood by studying the electrochemistry and hydrogen production of the reaction. A metal complex's ability to donate a hydride to a substrate of interest allows for major thermodynamic casual relationships and assumptions. [30-31] The information and determination of hydride transfer potential of the desired products can be used to contribute to an overall hydride donor ability scale and improve catalytic design in the future.

This report attempts to synthesize a cobalt-triphos catalyst that effectively hydrogenate acetone to isopropanol. Characterization reports of this metal is highlighted by this paper, and catalytic capability is measured electrochemically. For comparison, a nickel-triphos complex is synthesized, characterized, and measured electrochemically to assess the capability of these species to promote hydrogenation reactions.

Results and Discussion

Cobalt and nickel ions were coordinated with the tridentate phosphine ligand, triphos, and the resulting species were studied *in situ*. The efficacy of the cobalt complex as a catalyst for the hydrogenation of acetone to isopropanol was determined by electrochemical observations by cyclic voltammetry.

In an air-free reflux reaction, the cobalt (II) aqua ion was combines with the triphos ligand in a 1:1 ratio, forming a pink solid. This complex was then reduced with $NaBH_4$ in attempt to form the cobalt (I) hydride complex, $[HCo(triphos)]BH_4$. The pink crystals were purified by layered recrystallization and isolated by evaporation. This product of the initial synthesis was characterized by NMR spectroscopy (spectrum found in supplemental information), optical spectroscopy, and cyclic voltammetry. The product was found to be contaminated with $NaCl/NaBH_4$ salts and required further recrystallization and purification.

Despite the isolated product being a similar color to that described in literature, the synthesized product's NMR spectrum does not match the cobalt-triphos spectrum reported by Marinescu. The Marinescu report characterized several species believed to contribute to the electrocatalytic production of hydrogen by cobalt triphos species. Our attempted reproduced species of the hydride species was unsuccessful, as determined by NMR and optical spectroscopy. We expect that the ligand signals in the NMR spectrum should be similar on the Co(I)ion, regardless of solvent coordination or hydride ligand coordination. While the hydride ligand would result in some changes to the NMR spectrum, the expected triphos signals described by Marinescu were not exhibited in the NMR spectrum of the synthesized product. We expected the hydride complex to be a diamagnetic, square planar, d^8 species that displayed some similarity to the NMR spectrum found by Marinescu. The spectrum, however, is suspected of being paramagnetic due to the broadening in the NMR spectra.

Furthermore, the hydride signal, expected upfield of -5 ppm, should have been a doublet of triplets, but was not found in the NMR spectrum. Due to the electron density of metal complexes, as well as the hydride ligand's proximity to the metal center, the metal-hydride complex results in an up-field chemical shift in the ^{1}H NMR spectrum.[32] This would suggest that the initial synthesis of HCoTriphos was unsuccessful. Alternatively, as described earlier, the suspected paramagnetic nature of the product could have resulted in the NMR signal for the hydride ligand to be broadened such to be unobservable.

The NMR was performed in deuterated acetonitrile due to a color change from red to blue when dissolved in deuterated chloroform. This observation may suggest that the hydride complex was successfully synthesized as halogenated solvents have been shown to replace hydride ligands with chloride ligands.

In order to optimize the synthesis and minimize decomposition reactions, a second synthesis reaction was carried out using the same method as the initial synthesis but refluxate room temperature as opoosed to the high temperature reflux conditions. This red product did not form crystals, instead producing a red film, suggesting that the second synthesis produced an impure product. The NMR spectrum was also starkly different from that found in literature, suggesting that the cobalt-triphos complex was not successfully synthesized.

Both products were characterized by optical spectroscopy (shown in **Figure 4)**. Both shared the same λ_{max} (at 510 nm), but this did not match the wavelength found by Marinescu for a similar species at 320 nm and 820 nm.

The matching optical spectroscopic signatures of the two synthetic procedures suggest that the product formation was reproducible, however, without crystallographic or irrefutable spectroscopic data to confirm the identity of the species, no conclusive characterization can be made. The spectroscopic data did not match those reported by Marinescu, confirming that the synthesized material was not the desired cobalt (I) triphos hydride complex.

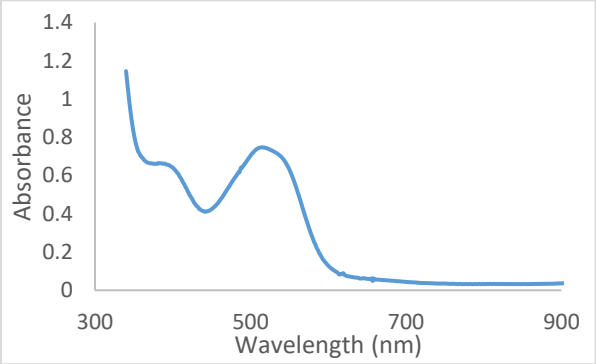

Figure 4. The UV-Vis of the synthesized Co-Triphos complex.

To minimize decomposition reactions and allow formation of a reproducible result, cyclic voltammogram experiments were performed using cobalt species generated *in situ*. The multi-dentate nature of the ligand prevents formation

of a complex with more than one triphos ligand, so the *in situ* experiments were likely to improve the solvent-bound Co(triphos) complex. Further, these experiments were carried out without an internal reference such as ferrocene, as the complex itself has a reversible wave near the same potential. These overlapping signals prevented the use of the standard electrochemical reference (cyclic voltammetry data is compiled in supplemental information)

A cyclic voltammogram was recorded with the crystals produced by the first synthesis. This showed a reversible wave near 0.5 V. Likewise, the *in situ* experiment showed a similar curve in which the two shared similar waves at 0.5 V. This suggests that the *in situ* experiments were generating the same species found in the initial syntheses with isolated products.

Upon the addition of excess p-toluenesulfonic acid (10x the molar equivalent of the metal) the cyclic voltammogrammetry experiments recorded an increase in the current consistent with Marinescu's observed hydrogen production. However, the electrochemical couple shifted from 0 V to 0.5 V in these experiments.

Acetone was then added by syringe to the experiment, and this caused an even greater increase in current (**Figure 5)**. Following the addition of acetone, the current increased by 1000-fold. This extreme increase suggests that the cobalt-triphos complex serves as an efficient and possible catalyst for acetone.

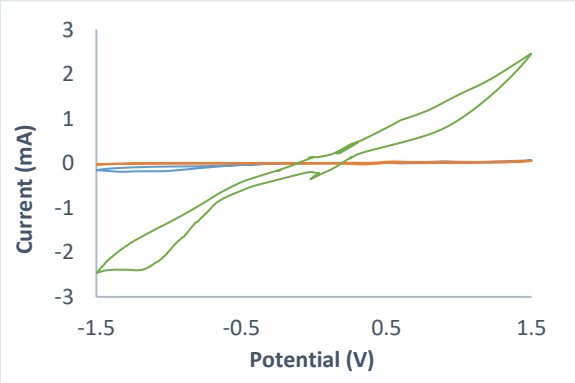

Figure 5. The CV of Co + Triphos in situ prep. The orange line is that of cobalt + triphos, the blue of cobalt + triphos + p-Toluenesulfonic acid, and green of cobalt + triphos + p-Toluenesulfonic Acid + acetone. Notice the stark increase in current after acetone was added, supporting that the cobalt-triphos complex successfully hydrogenates the C-O double bond of acetone.

Due to restrained time and resources, future experiments would call for measuring the rate and amount of isopropanol produced by the hydrogenation of the acetone. This would support the argument for the metal complex's catalytic abilities. However, the data collected by the cyclic voltammograms do show promising results for the catalytic ability of cobalt-triphos compounds for the acetone hydrogenation reaction. Moreover, the hydricity of these could allow for the characterization of the thermodynamics of single electron or single proton changes to the metal complex.

The corresponding nickel triphos complex was also of interest in this study as a point of comparison. The species was synthesized *in situ*, and the electrochemistry of this species was compared with the cobalt-triphos complex. Tge hydricity of tridentate nickel phosphine complexes have been studied extensively,[33] the comparison with the tridentate phosphine (triphos) specie would be welcome.

However, in our studies, the nickel triphos species shows less promising results as a useful and efficient catalyt for the transformation of acetone to isopropanol.

Similar to the attempted synthesis of Co(triphos), the hydride peak was not observed in the NMR spectrum for the desired $[Ni(triphos)H]^+$ complex. However, recorded spectrum for the synthesized nickel complex does correlate with that found in literature for a similar species. This suggests that the nickel complex synthesized is related to that found by Kourkine and associates, but it cannot be confirmed to be the desired nickel complex. Literature data for optical spectroscopy was not found for HNiTriphos.

The cyclic voltammogram of nickel and triphos, nickel with triphos and p-toluenesulfonic acid, and nickel with triphos, p-toluenesulfonic acid, and acetone showed fewer potential differences than the cobalt complex

(**Figure 6**). This suggests that the cobalt coordinated complex serves as a better catalyst for the hydrogenation of acetone than nickel does. This may be due to the difference in redox states that are possible for the two metals and the available space for the metal to promote hydrogenation. The hydrogenation of acetone to isopropanol by the nickel-triphos catalyst is likely slower and may have a lower overpotential.

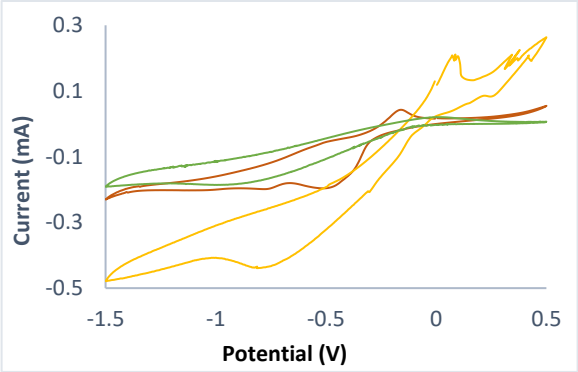

Figure 6. The CV of Ni + Triphos in situ prep. The green line is that of nickel + triphos, the red of nickel + triphos + p-Toluenesulfonic acid, and yellow of nickel + triphos + p-Toluenesulfonic Acid + acetone. Notice that the increase in current after acetone was added is much lower when compared to the increase by cobalt.

Experimental Section

Air-free chemistry was carried out in a Vac Atmospheres Genesis glovebox outfitted with both O_2- and H_2O- removal cartridges. NMR spectroscopy experiments were carried on a 60 MHz permanent magnet running on Anasasi software. The UV- Vis spectrometer was produced by Agilent. Cyclic Voltammetry experiments were carried out using a portable potentiostat manufactured by PineWave Now.

HCoTriphos. *Initial synthetic attempt.* A dark red solution of $Co(OH_2)_6(BF_4)_2$ (0.3443 g, 1 mmol) in ethanol (10 mL) was combined with a colorless solution of triphos (0.53 g, 1 mmol) in acetone (~20 mL). $NaBH_4$ (0.15 g, 4 mmol) dissolved in ethanol (5 mL) was added to the $NaBH_4$ vial was slowly added to the cobalt reaction flask (chilled on ice in the fume hood and fitted with a condenser), resulting in a darker red color. The flask stirred on ice for 1.5 hrs.

The flask was then brought to reflux for 1 hr, then the solvent was removed on a rotary evaporator. The dark red solid was then recrystallized with layers of pentane and THF. This resulted in pink crystals. Precipitated sodium tetrafluoroborate was removed by filtration through glass wool. Isolated product: 0.2756 g, 0.46 mmol, 46.36% yield based on mole ratio of cobalt. UV-Vis (acetonitrile, 480 nm): λ_{max} at 510 nm. H^1-NMR ($CDCl_3$, 60 MHz): 0.61 ppm (s), 2.10 ppm (d), 7.01 ppm (d). *Second synthetic attempt.* The second synthesis began in the same manner, using $Co(OH_2)_6(BF_6)_2$ (0.3409 g, 1 mmol), triphos (0.53 g, 1 mmol), and $NaBH_4$ (0.15 g, 4 mmol) in the same respective solvents. This synthesis was not heated and remained on ice for 1 hr. The resulting product was a red gluey solid. The product was dissolved in pentane and the solvent was removed on a rotary evaporator, resulting in a red film. This product was layer recrystallized with THF and pentane. Isolated product: 0.2464 g, 0.41 mmol, 31.45% yield based on mole ratio of cobalt. UV-Vis (acetonitrile, 480 nm): λ_{max} at 510 nm.

Catalysis. A number of cyclic voltammetry experiments were performed with these products in 0.25 M [*n*-Bu_4N][PF_6] in THF. The subsequent experiments were performed *in situ*, in which the $Co(OH_2)_6(BF_6)$ (~0.34 g, ~0.1 mmol) and triphos (~0.53 g, ~0.1 mmol) were added to the vial directly. Ferrocene was not used in the CV experiments. p-toluenesulfonic acid (~0.19 g, 1mmol) was then added to the vial. Via syringe, acetone (0.7 mL to 400 µL) was added to the vials to study catalysis.

HNiTriphos. Synthesized in same way as second synthesis of HCoTriphos using $Ni(OH_2)_6(BF_6)_2$ (0.3402 g, 1mmol), triphos (0.51 g, 1.5 mmol), and $NaBH_4$ (0.15 g, 4 mmol). The product was a dark orange solid. Catalysis testing was done with the *in situ* technique. Isolated product: 0.2145 g, 0.36 mmol, 36.04% yield based on mole ratio of

nickel. UV-Vis (acetonitrile, 480 nm): λ_{max} at 415 nm. H^1-NMR ($CDCl_3$, 60 MHz): 2.01 ppm (m), 3.98 ppm (s), 4.05 (m), 9.01 (m).

Conclusion

The promising results of the *in situ* cobalt-triphos cyclic voltammogram experiments suggest that the cobalt catalyst may promote for the hydrogenation of acetone. Future work to assess the actual viability of this catalyst is needed.

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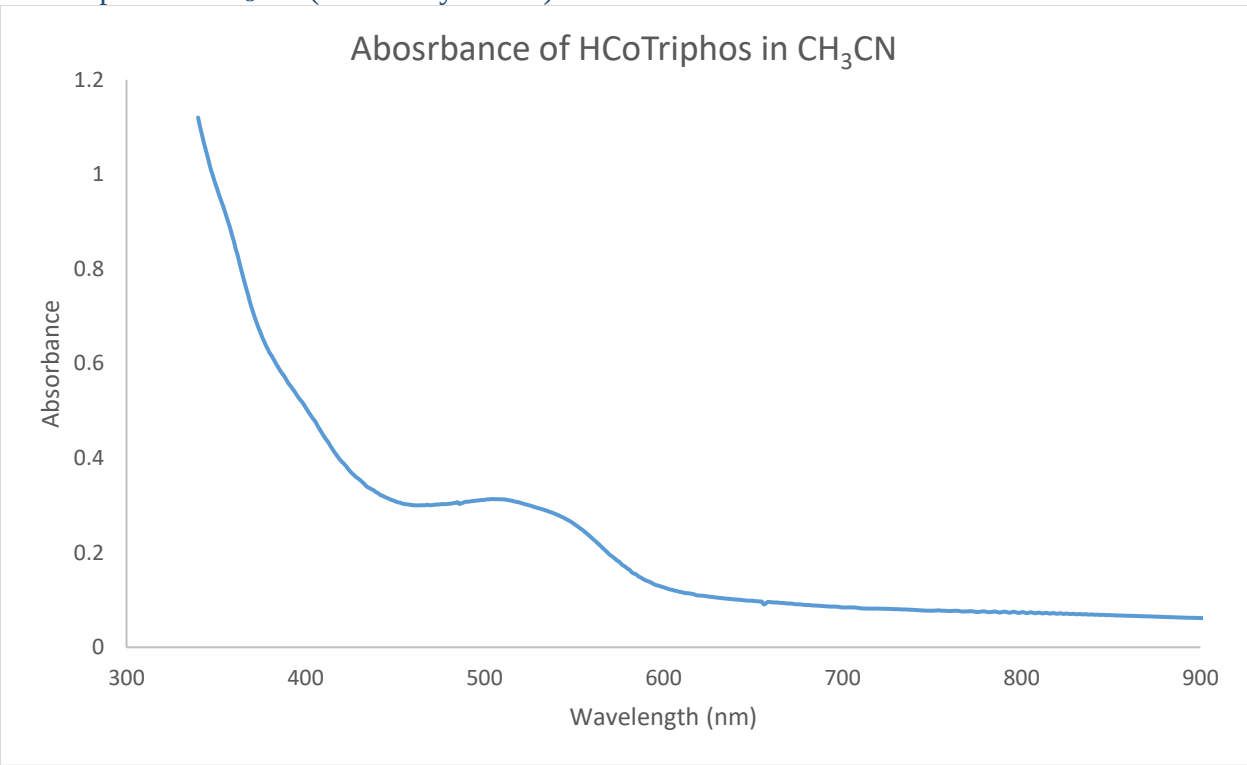
Supplemental Information

UV - Vis

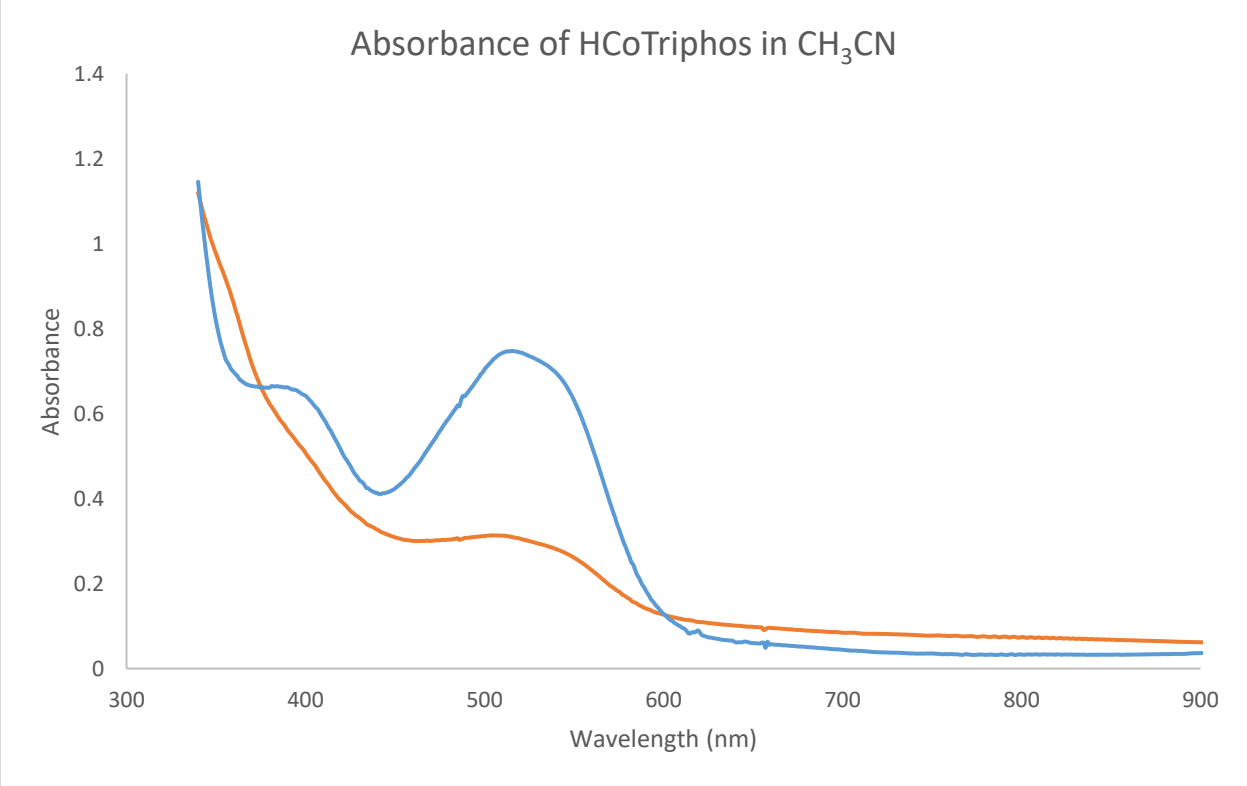
NMR

Cyclic Voltammograms

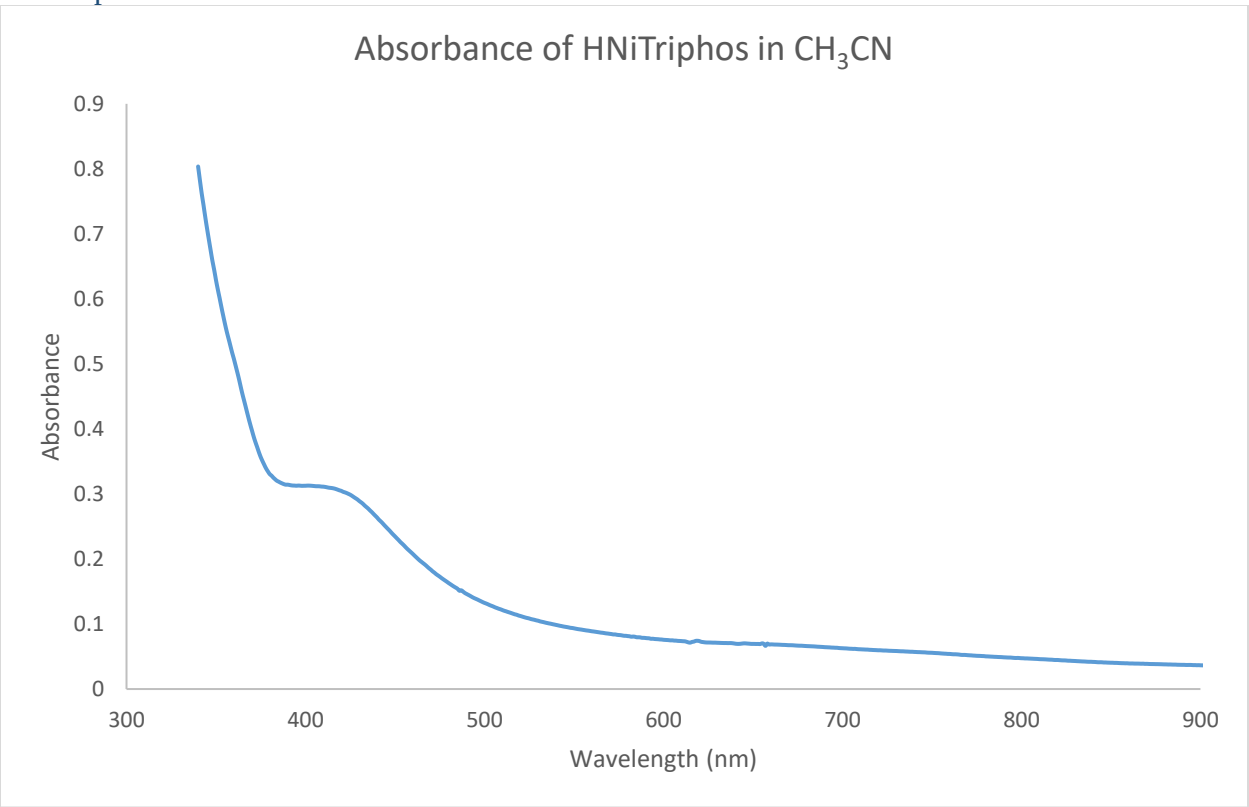
HCoTriphos in CH_3CN (Second Synthesis)



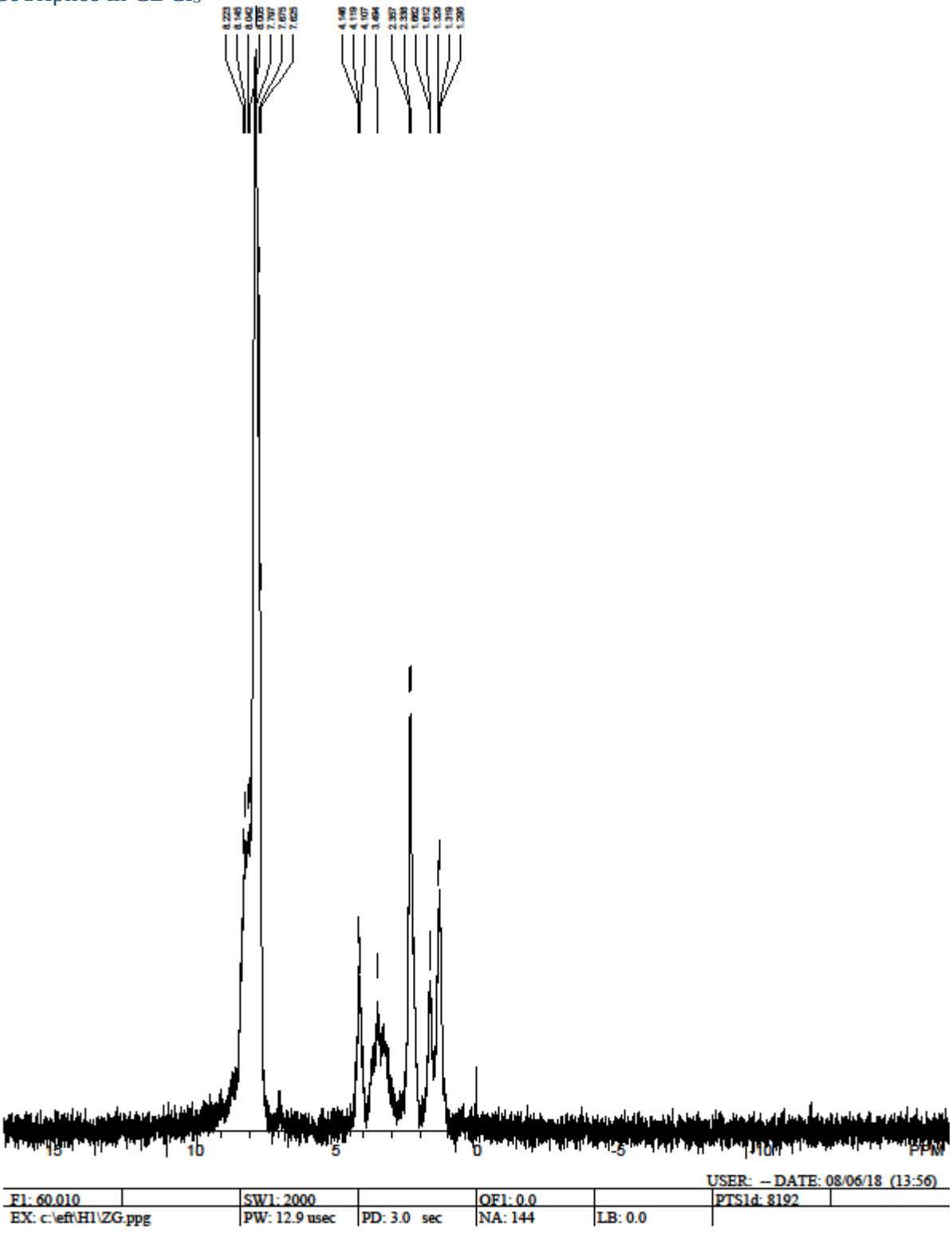
Juxtaposed UV-Vis Spectra of Both HCoTriphos Syntheses



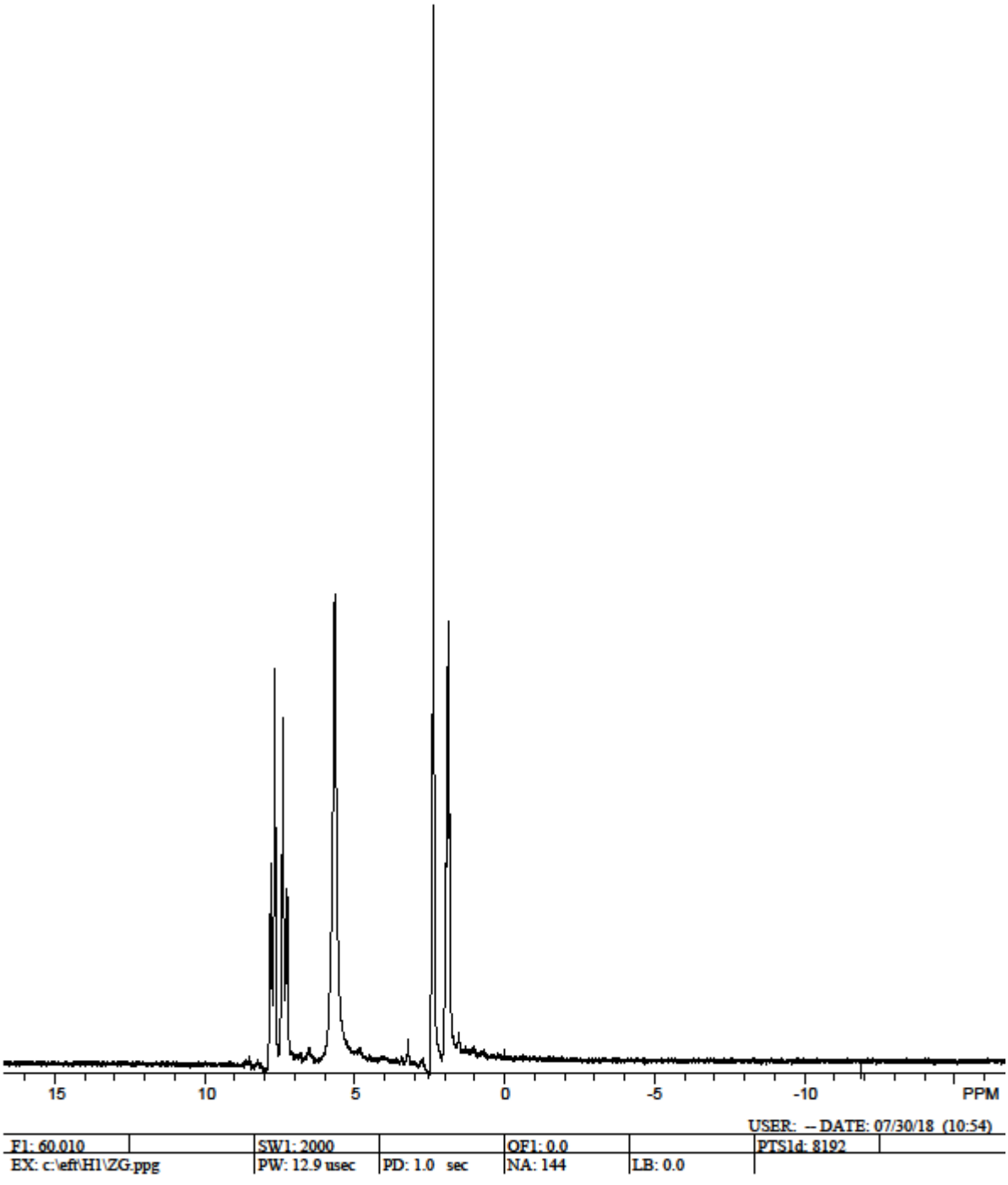
HNiTriphos


Absorbance of HNiTriphos in CH_3CN
Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
400
500
600
700
800
900
Wavelength (nm)

HCoTriphos in $CDCl_3$

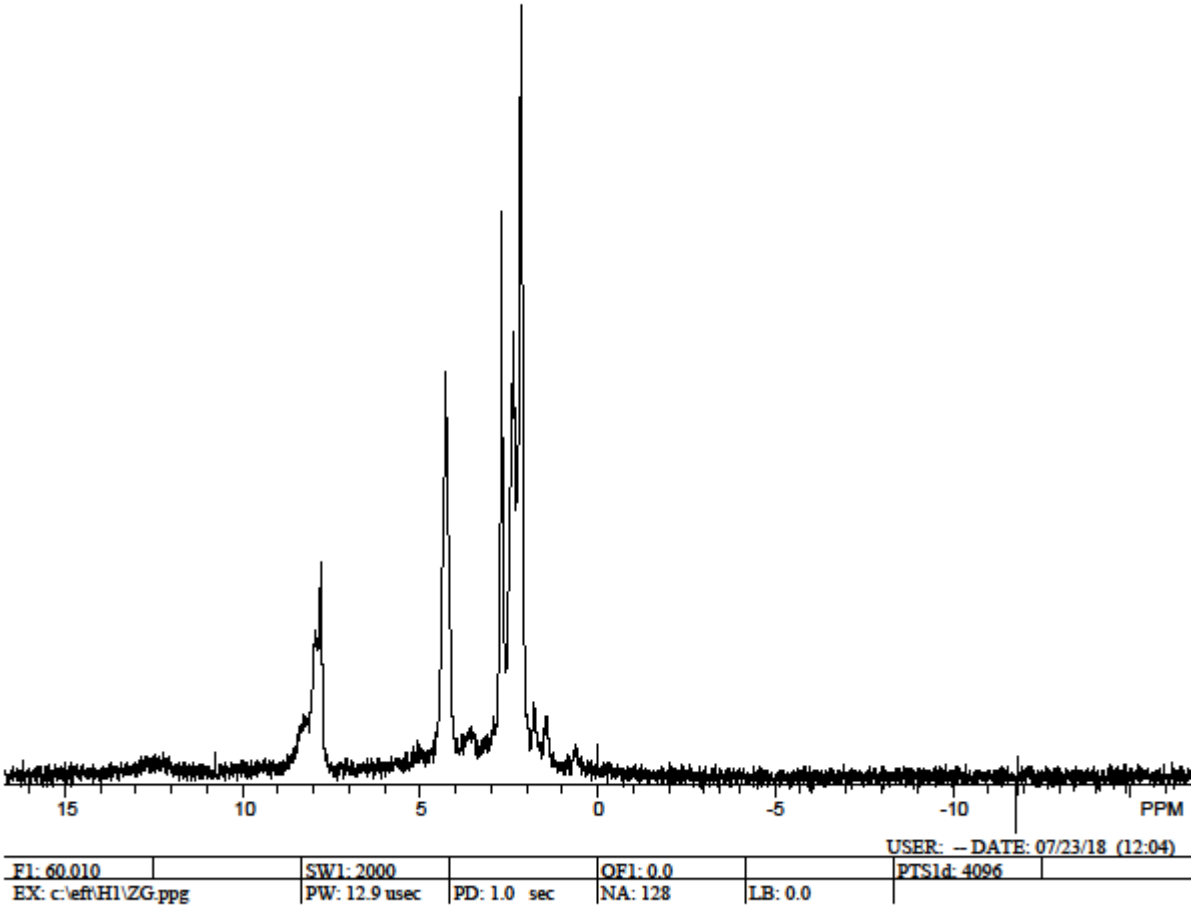


HCoTriphos in Acetonitrile-d3



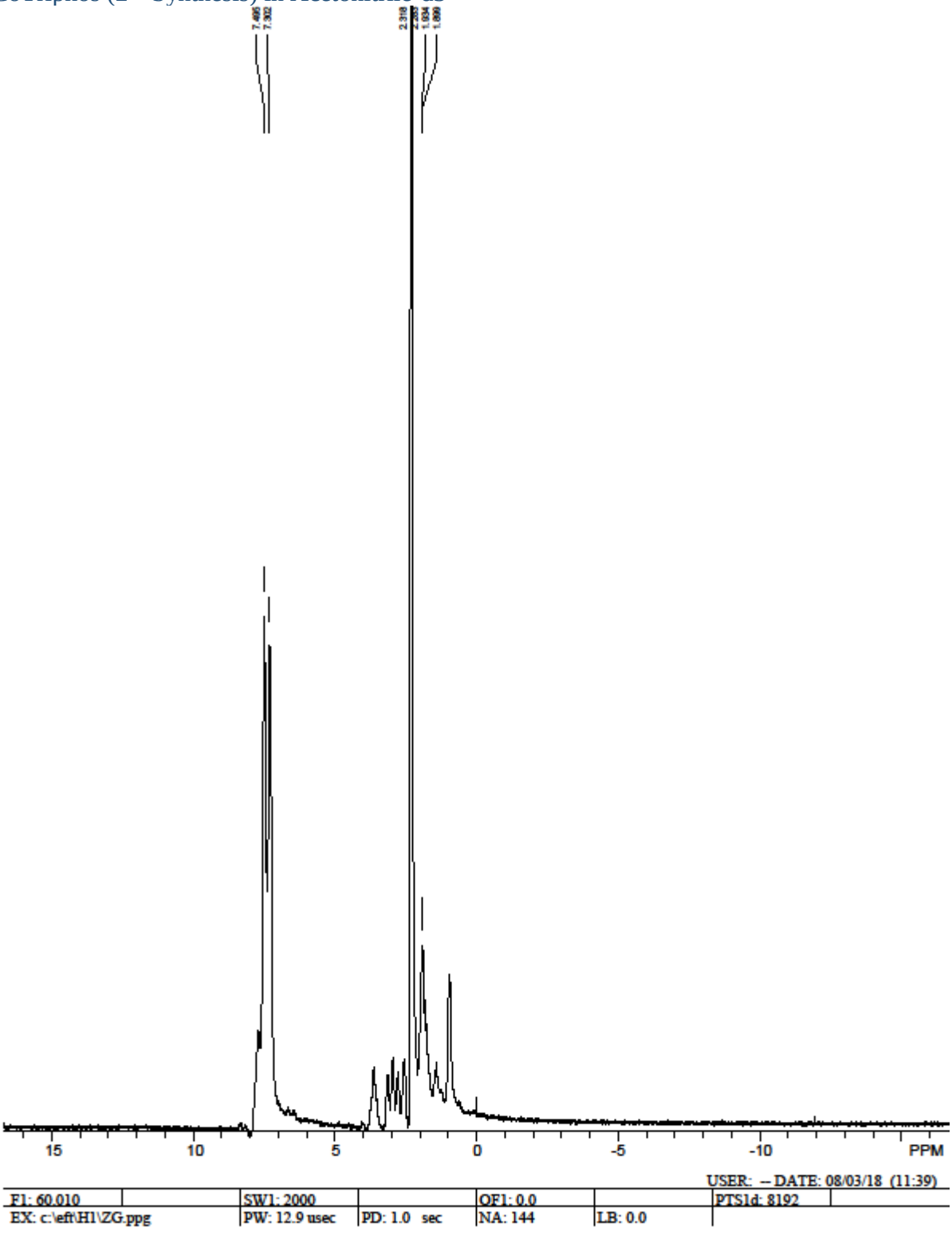
Acetonitrile

HCoTriphos in Acetonitrile-d3 Filtered through Glass Wool

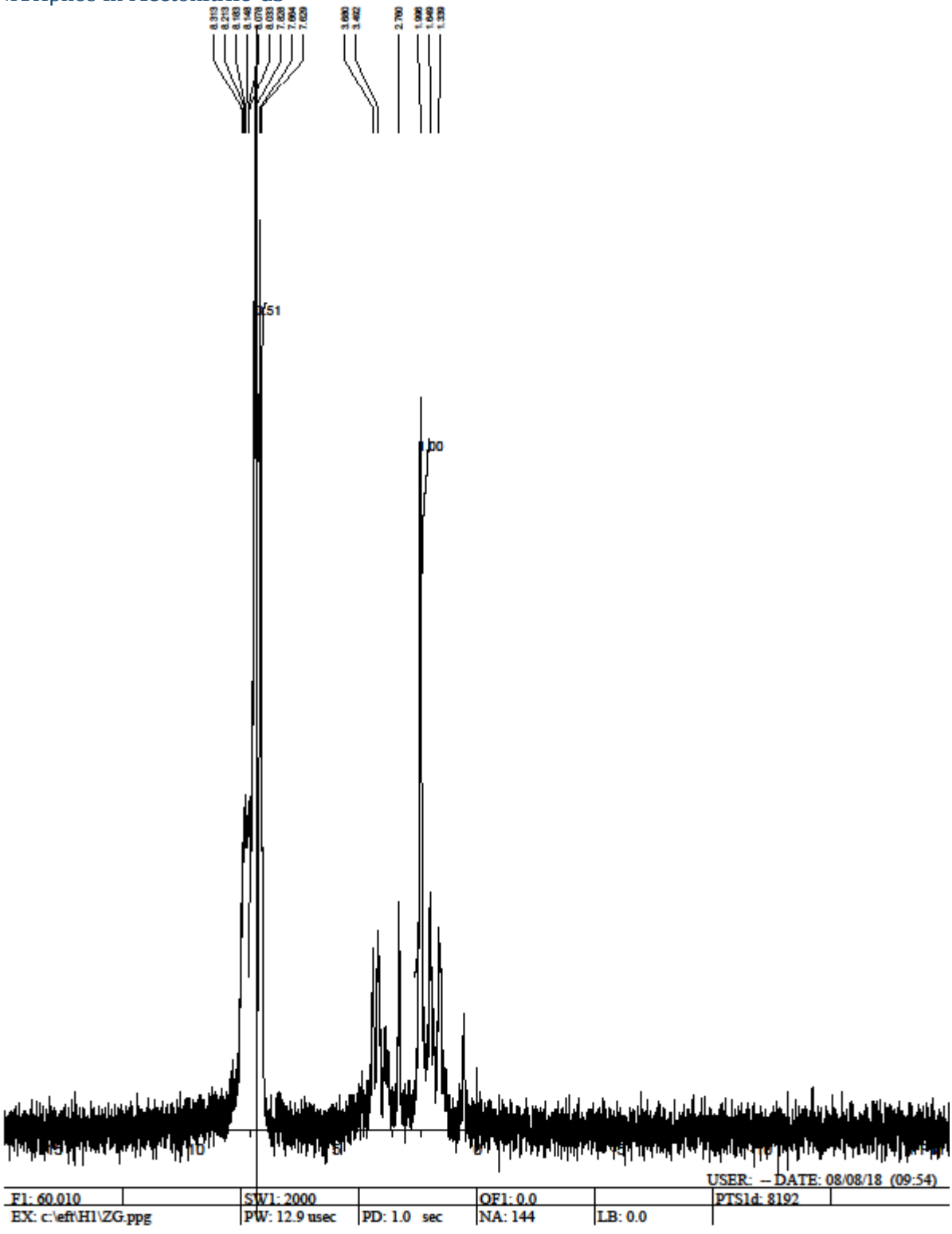


Glass wool

HCoTriphos (2nd Synthesis) in Acetonitrile-d3

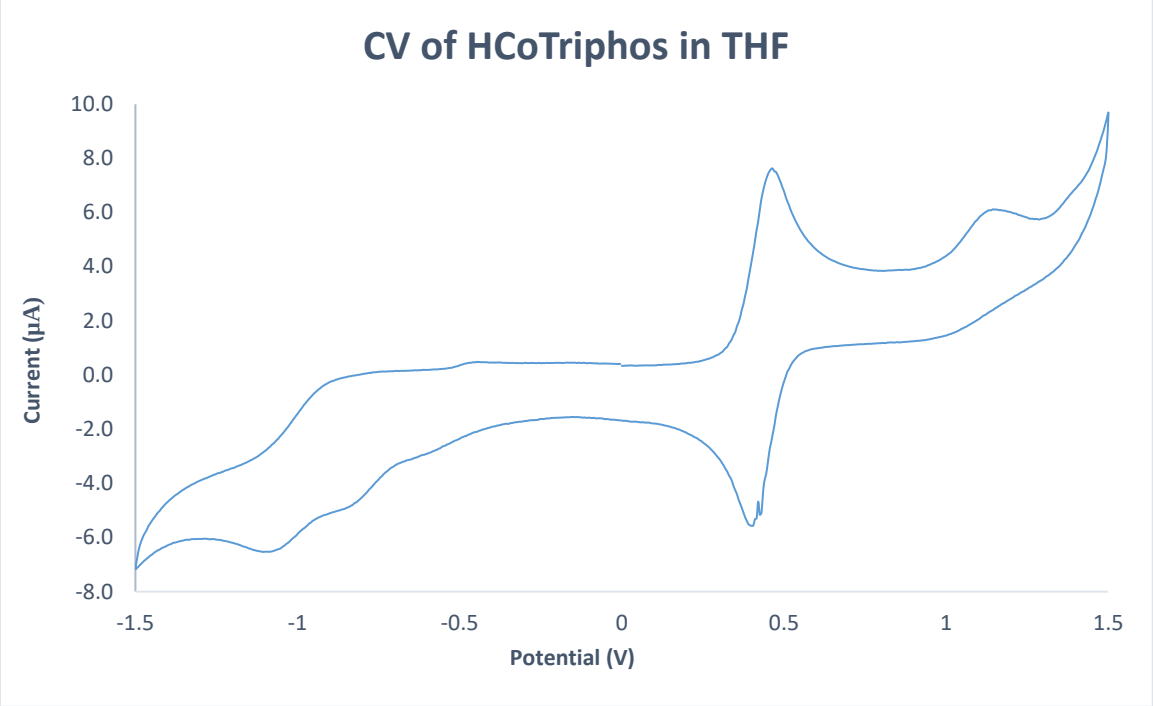


HNiTriphos in Acetonitrile-d3

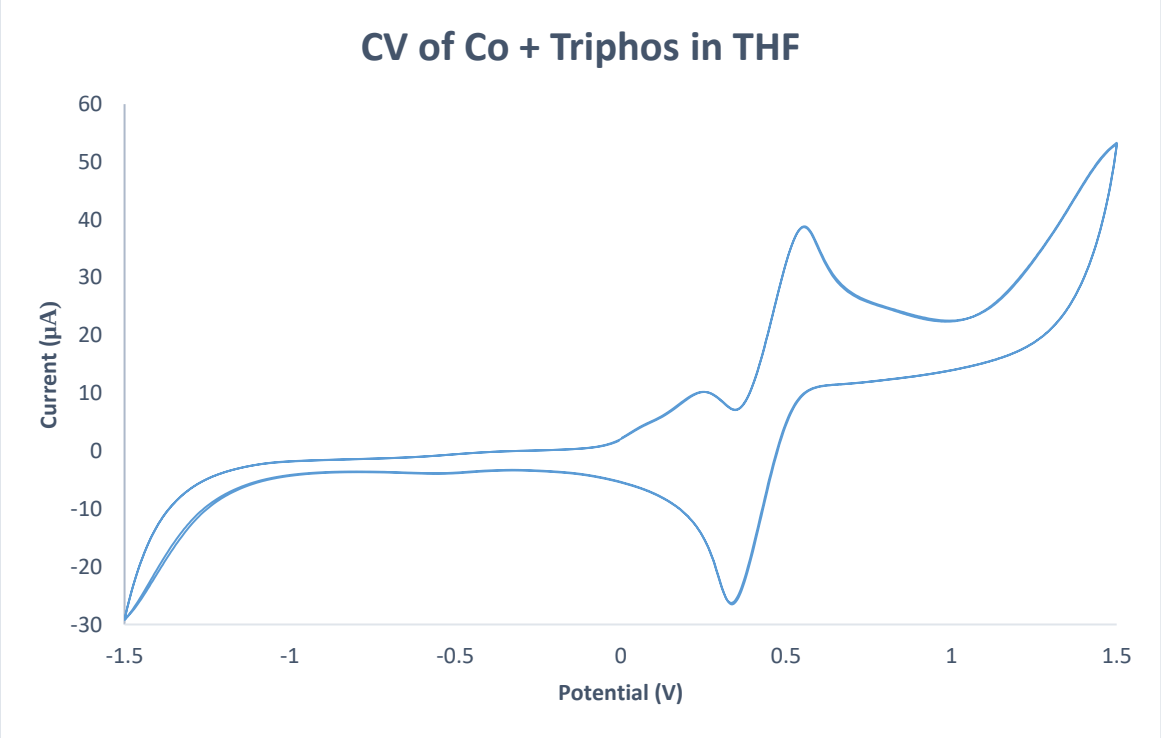


Hnitriphos

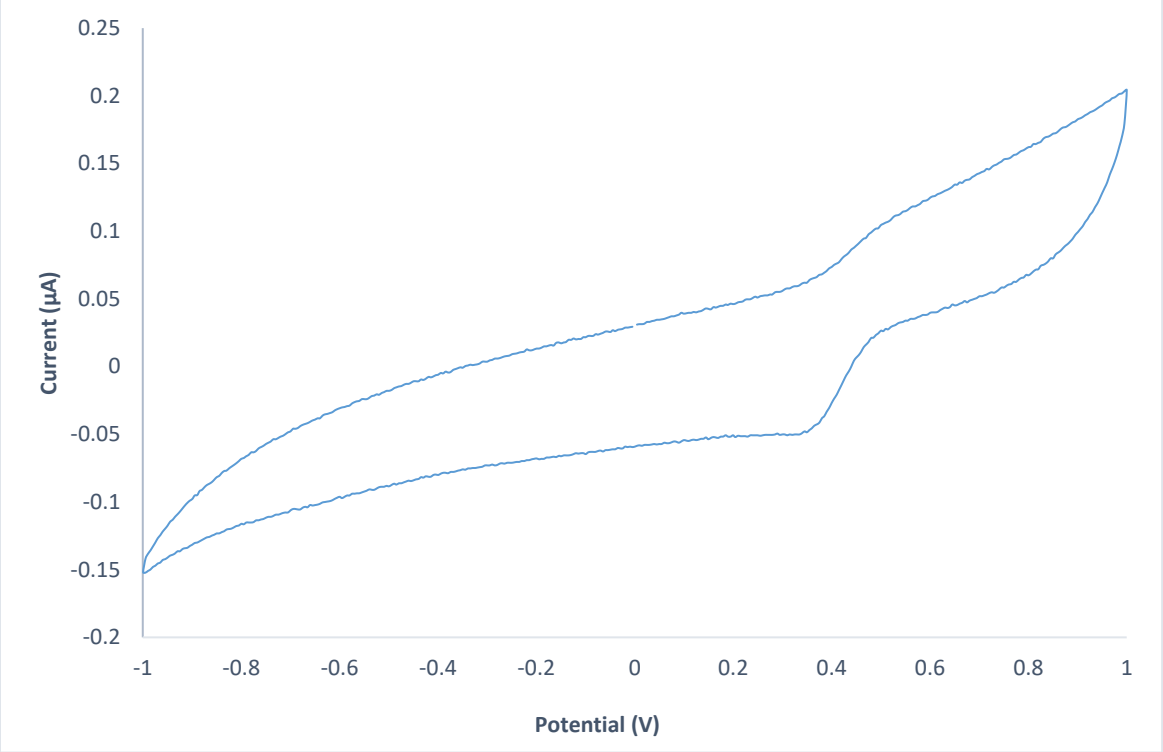
HCoTriphos (initial synthesis) in THF



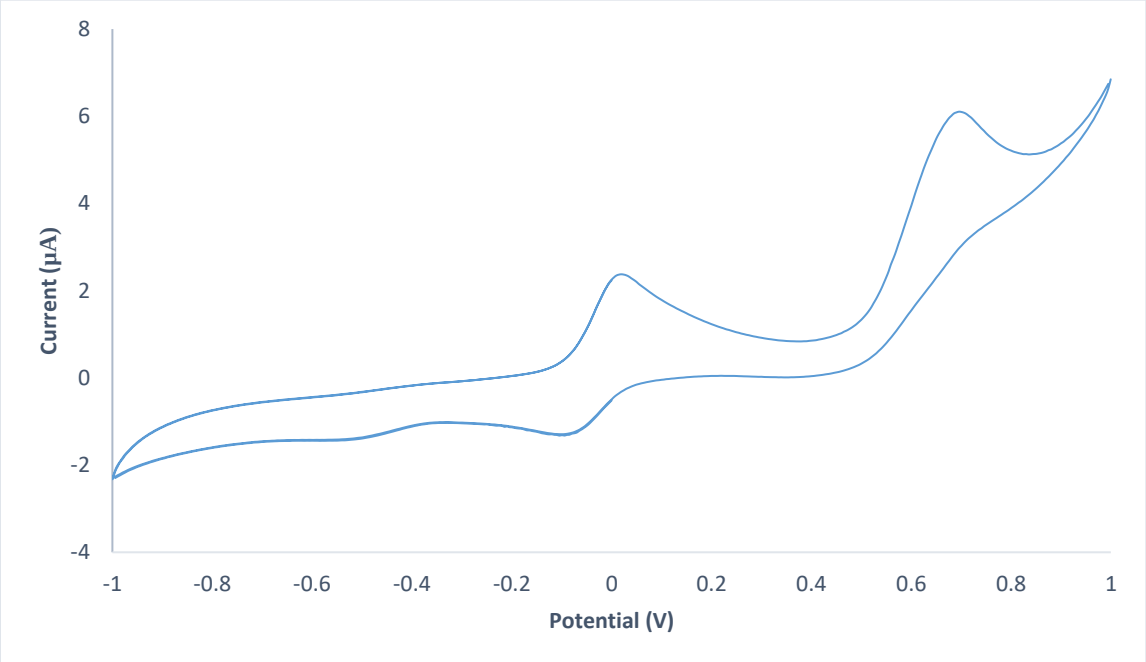
Co + Triphos (*in situ*) in THF



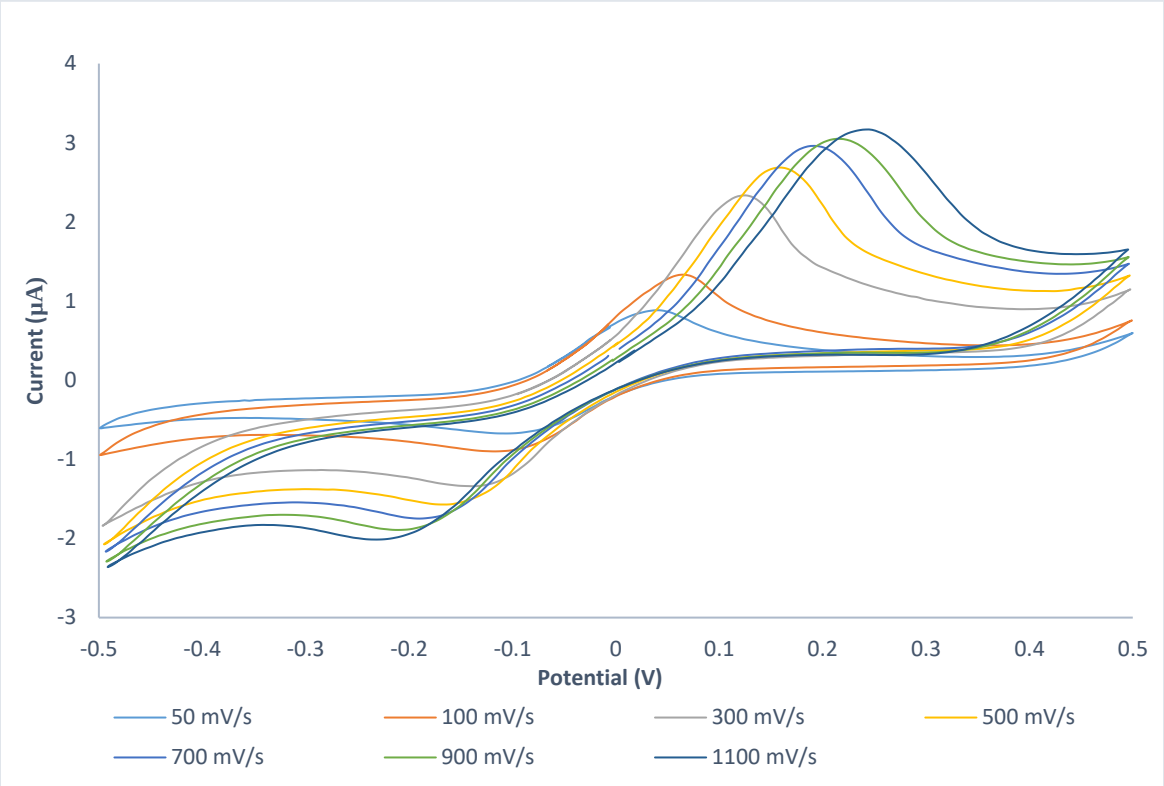
Co + Triphos with Ferrocene in THF



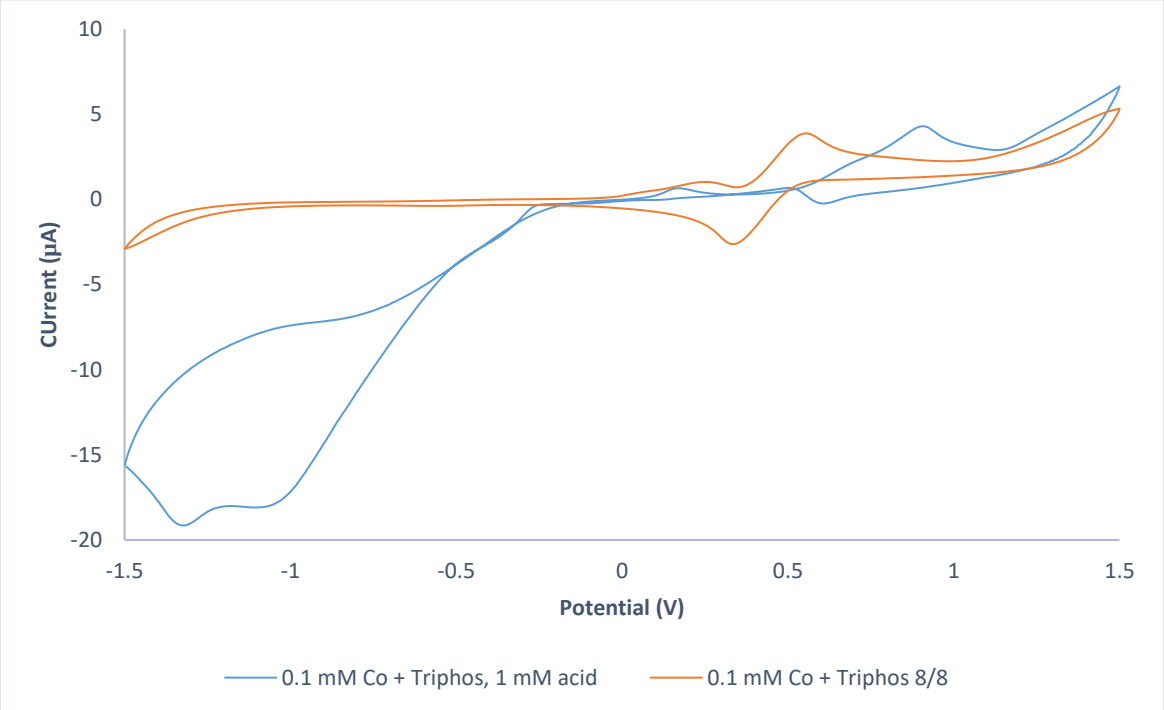
Co + Triphos in THF



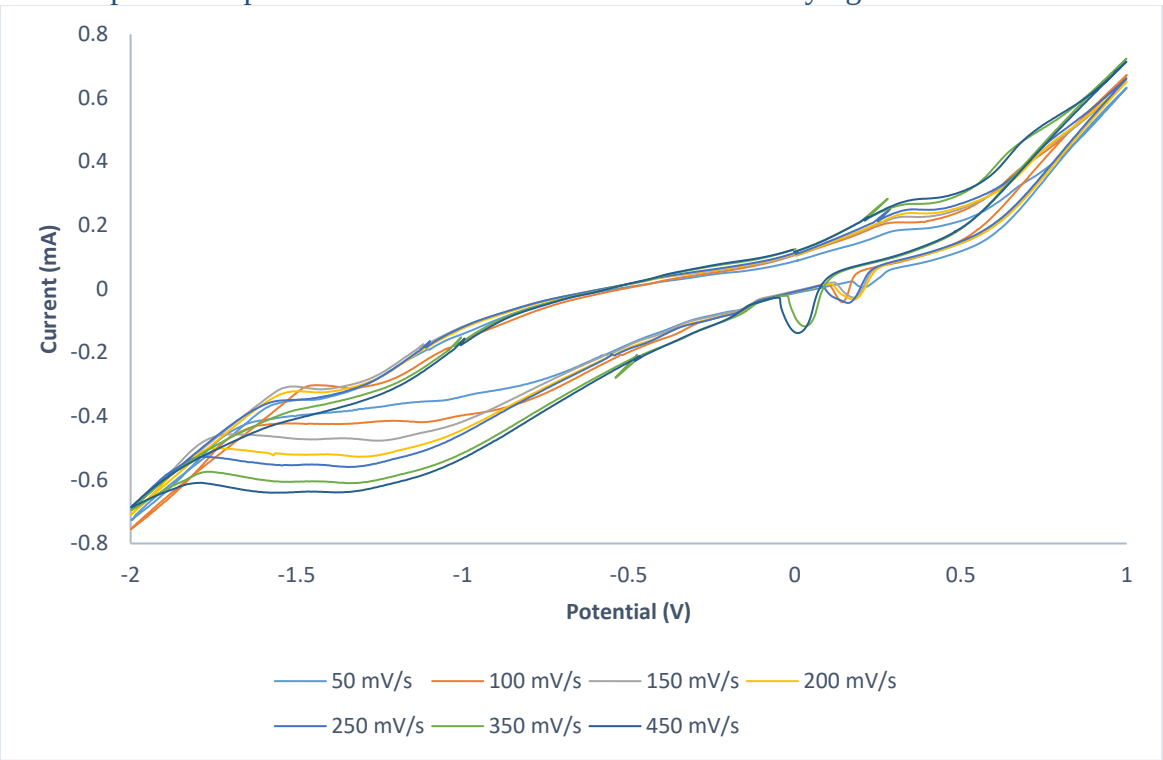
Co + Triphos at Varying Scan Rates



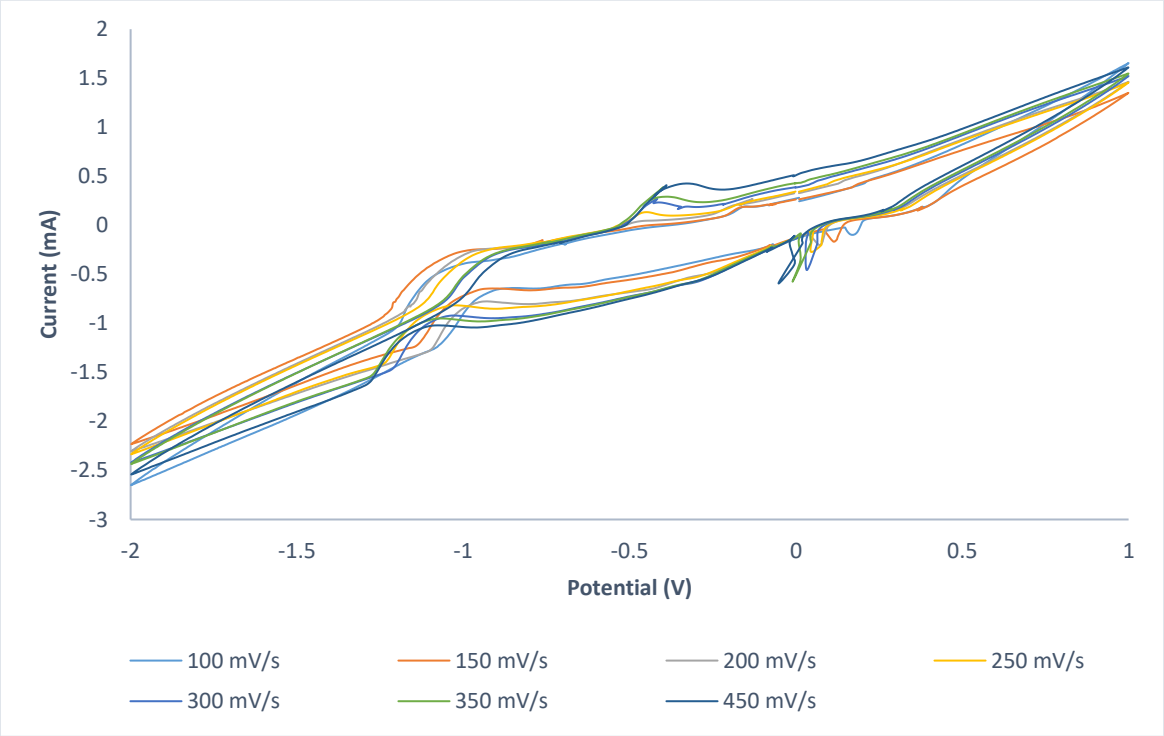
Co + Triphos versus Co + Triphos + p-Tolunesulfonic Acid in THF



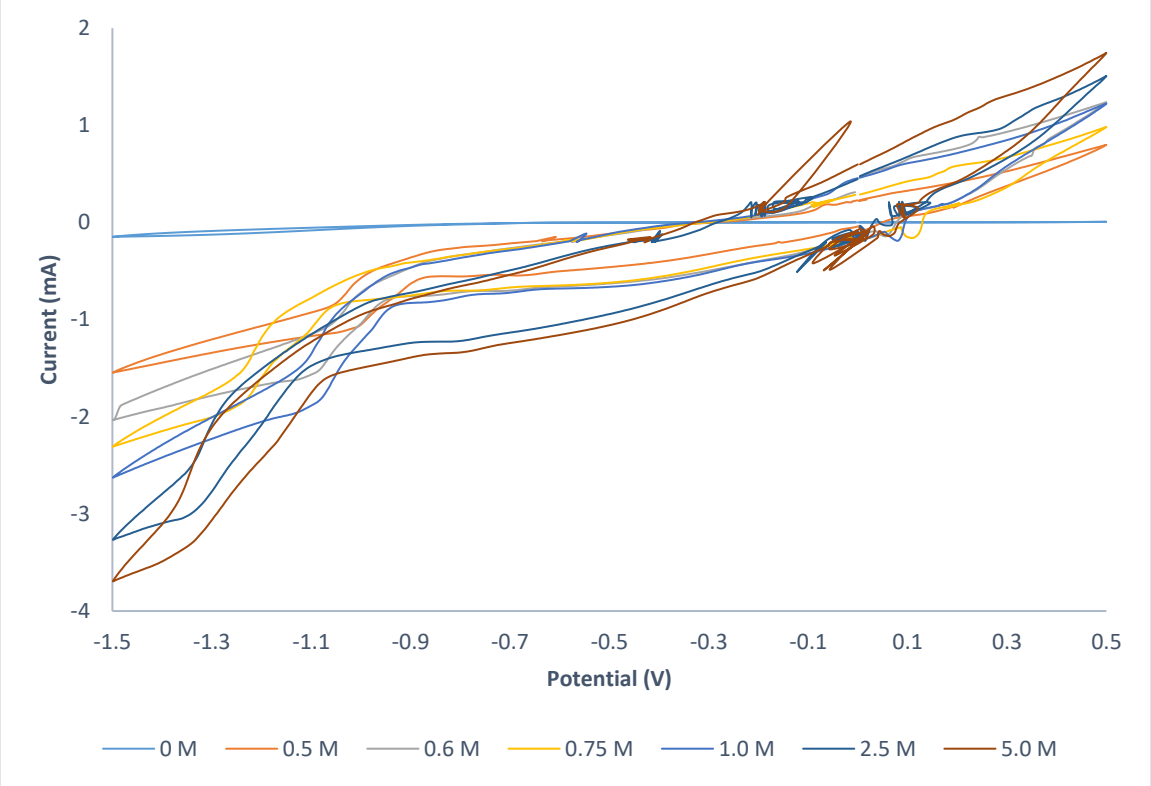
Co + Triphos with p-Toluenesulfonic Acid and Acetone at Varying Scan Rates in THF



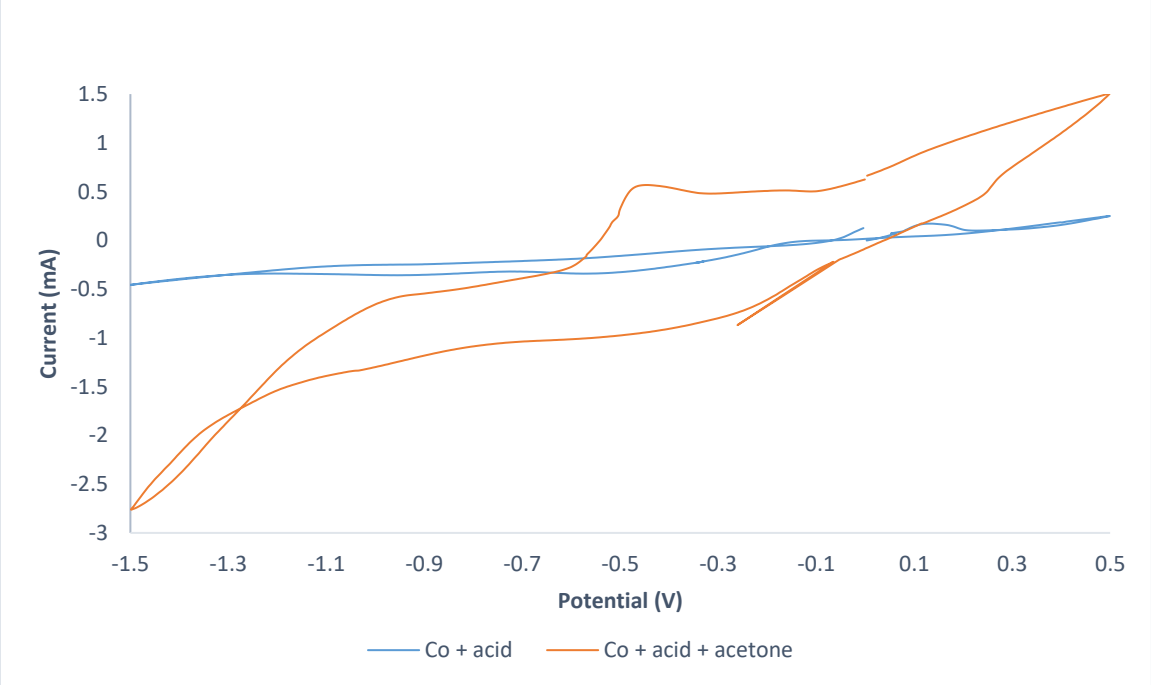
Co + Triphos with p-Toluenesulfonic Acid and Mixed Acetone at Varying Scan Rates



Co-Triphos with p-Toluenesulfonic Acid and Varying Scan Rates of Acetone

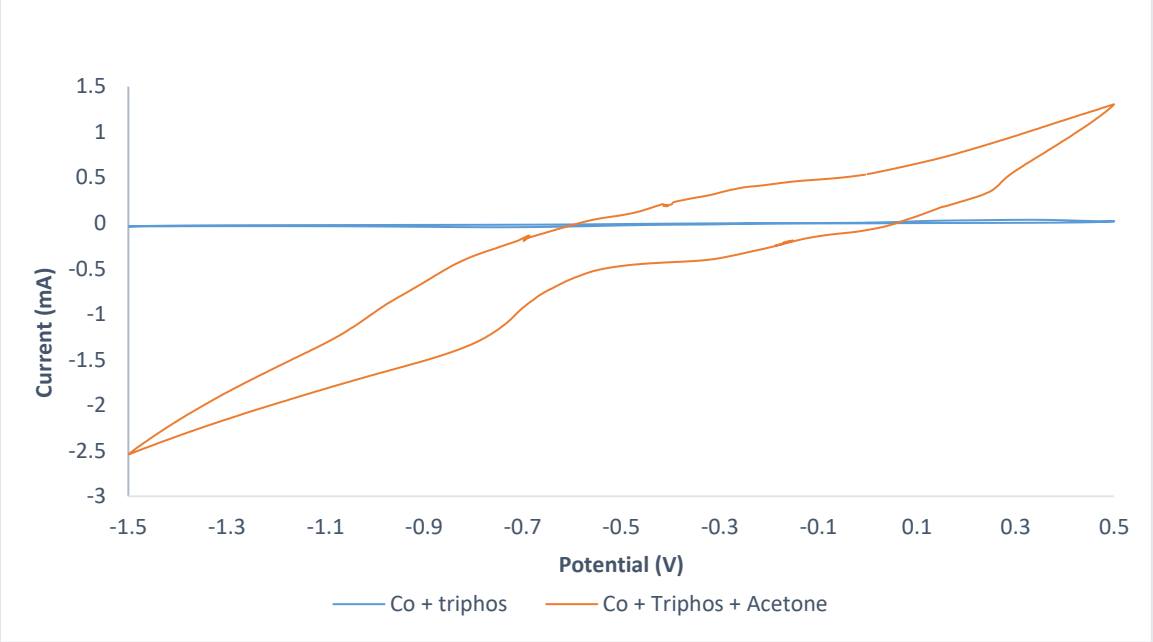


Cobalt with p-Toluenesulfonic Acid and Acetone

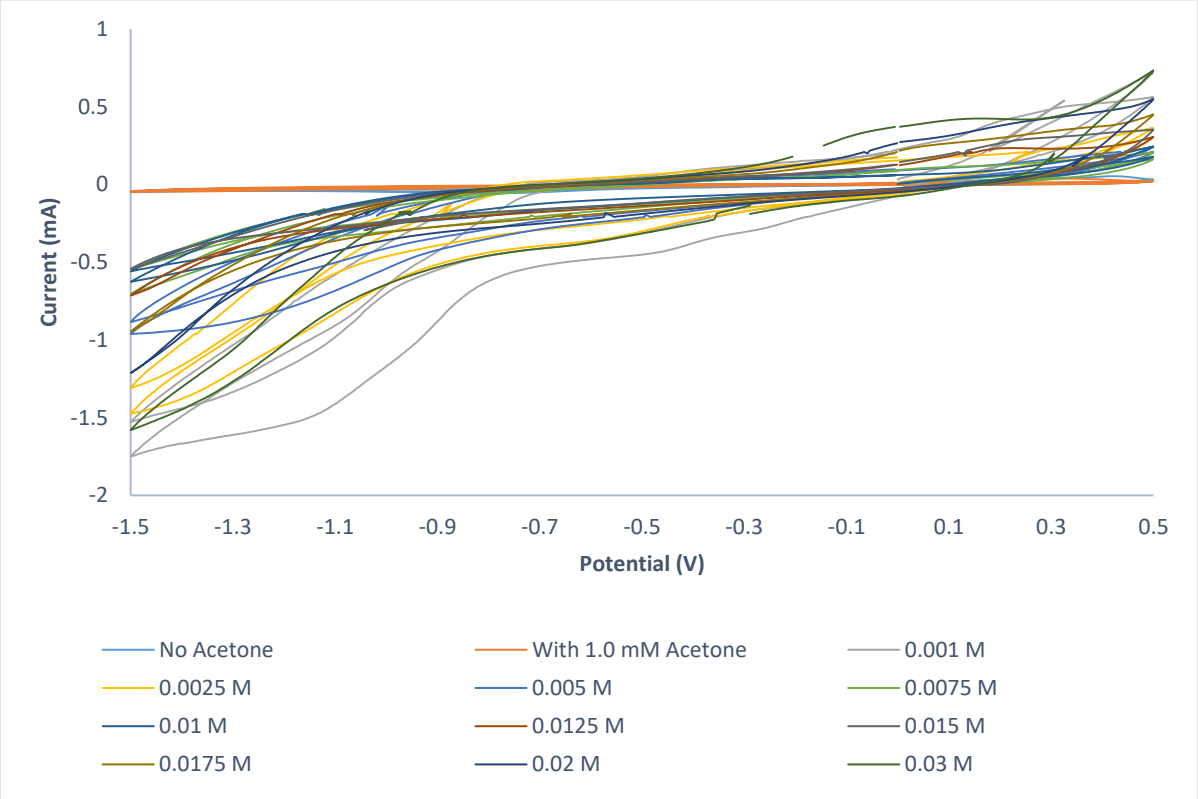


It seems as if the electrode itself had systematic issues at this point of the project.

Cobalt with Triphos and Acetone



Cobalt + Triphos with Acetone and Varying Concentrations of p-Toluenesulfonic Acid



On Faith and Learning

We are called to be stewards of the Earth. From our creation, we are meant to care for the environment and the rest of God's work and be neighbors to nature. As we have dominion of the Earth, we are meant to seek ways to protect and cherish the gift of God's love. Seeking greener alternatives to current chemical processes is a way that we can fulfill humanity's purpose in creation.

The hope of this project is to promote ways that sustainable energy can be brought into reality and decrease the need for modes of energy or production that are harmful to the environment. The distant hope of this type of research is to use these catalysts to directly lessen that amount of pollution that enters the environment by converting it from the source. Through continued research and active study of chemistry like this, greener alternatives can be perfected, and we can fulfill God's call for us to care for the world. It is through our love for the environment that we can better understand God's own love and who our Lord is. We should sustain and love nature, as He does too. Through things like these, we can learn more about God and be more like Him.

As I study chemistry, I am continuously being reminded of how God must be present in order for the world to work in the ways that they do. I study in wonder of how God's perfection is reflected in the way that he created the world. As I study chemistry, I know that there must be a God in order for any of this to be possible.